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Mechanism of Photoinduced Changes in the Structure and Optical Properties of Amorphous As_2S_3

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We propose a mechanism of photostructural changes in amorphous As_2S_3 ($a\text{-As}_2\text{S}_3$) on the basis of *ab initio* molecular orbital calculations on clusters of atoms modeling the local structure of the amorphous system. We have found that trigonal AsS_3 pyramidal units can be transformed into a fivefold coordinated As site having four As-S bonds and one As-As bond via a photoionization process. This photoinduced coordination defect center exhibits a lower photoabsorption energy as compared with the usual pyramidal structure, explaining the observed photodarkening effect of $a\text{-As}_2\text{S}_3$.

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Amorphous semiconductors such as As-based chalcogenides show remarkable photoinduced changes in the optical properties upon band-gap or sub-band-gap illumination [1]. Such photoinduced changes have received much attention, especially for applications to switching, memory, and imaging devices [2]. Since the absorption edge shifts to lower energies on illumination, this phenomenon is commonly called the “photodarkening effect.” In addition to photodarkening, As-based amorphous chalcogenides show photoinduced electron-spin resonance [3,4], anisotropy [5], and volume expansion [6,7]. Although it has been suggested that (coordination) defects formed on illumination act as the cause of the observed photoinduced phenomena [1,8,9], a detailed microscopic understanding of the structural changes in amorphous chalcogenides upon illumination is still lacking.

One of the promising methods to get a better knowledge of the photostructural changes in amorphous solids is to use *ab initio* quantum-chemical calculations based on cluster models [10,11]. Fortunately, the localized electronic states near the band edges of amorphous semiconductors do not extend through the solids [12], and the photostructural changes in amorphous chalcogenides are hence mainly described by the local nature of excited electrons. Thus, photoexcited electrons and holes will end up in localized band-tail states having a longer lifetime than that in the corresponding crystals, leading to a different metastable state before recombination occurs. Thus, we consider that the *ab initio* cluster calculations are useful to investigate such localized electronic states in amorphous materials and may give new insight into the underlying mechanism of the observed photostructural changes.

In this Letter, we investigate the photostructural changes in amorphous As_2S_3 ($a\text{-As}_2\text{S}_3$) using clusters of atoms that model its local structure. There is general agreement that $a\text{-As}_2\text{S}_3$ has a layered structure similar to that of its crystalline counterpart ($c\text{-As}_2\text{S}_3$), orpiment [13]. Each layer comprises AsS_3 trigonal pyramids, which are connected

via shared S atoms at the respective vertices. It is reasonable to expect that the photoinduced processes involve structural rearrangements in both intralayer and interlayer configurations [8]. Thus, we have employed an $\text{As}_3\text{S}_8\text{H}_7$ cluster (model 1; see Fig. 1) as a model of the local structure of $a\text{-As}_2\text{S}_3$. The H atoms in the cluster are used to saturate the dangling bonds of “surface” S atoms. As shown in Fig. 1, this model is composed of two “freely floating” submolecules, namely, $\text{As}_3\text{S}_3\text{H}_3$ and $\text{As}_2\text{S}_5\text{H}_4$. The usage of the floating molecules is due to a simplification imposed by the limited computer power. However, the structural flexibility of $a\text{-As}_2\text{S}_3$, which indeed exhibits large photoinduced structural changes, can allow us to use such a simple cluster as a model of the intralayer as well as interlayer interactions in actual $a\text{-As}_2\text{S}_3$. The geometry of the cluster was fully optimized at the Hartree-Fock (HF) level with the 6-31G(d) basis set [14]. All *ab initio* molecular orbital calculations in this work were performed using the GAUSSIAN 98 computer program [15].

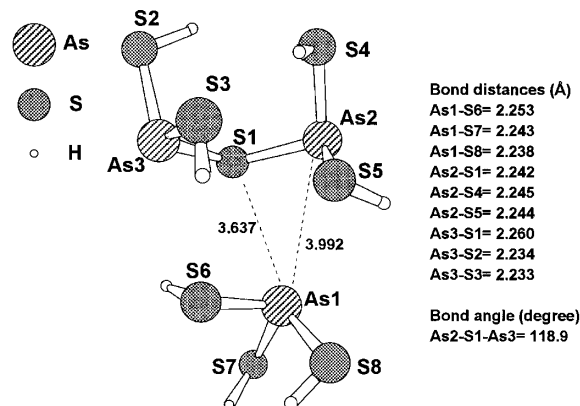
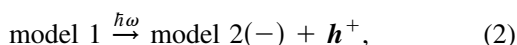
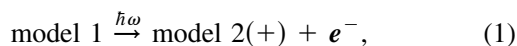


FIG. 1. Optimized geometry of the $\text{As}_3\text{S}_8\text{H}_7$ cluster, model 1, calculated at the HF/6-31G(d) level. Principal intramolecular and intermolecular (dashed lines) distances and bond angle are shown. The average intramolecular As-S bond distance is 2.243 Å.

The optimized geometry of model 1 calculated at the HF/6-31G(d) level is shown in Fig. 1. Previous extended x-ray-absorption fine-structure measurements have demonstrated that the average As-S bond distance, $d_{\text{As-S}}$, observed for annealed α -As₂S₃ films is 2.280 Å [16]. This observed bond distance is in reasonable agreement with the average As-S bond distance ($d_{\text{As-S}} = 2.243$ Å) calculated for model 1. However, the calculated As2-S1-As3 bond angle in model 1 (118.9°) is larger than the observed value (100.3°) for annealed α -As₂S₃ films [16]. In addition, the nonbonding As-As contribution between the two submolecules in model 1 is calculated to be ~ 4 Å, which is appreciably longer than that in the interhelix As-S-As linkages in c -As₂S₃ (3.19 Å [16]). This discrepancy is probably due to the usage of the floating molecules, which neglect long-range strains and weak van der Waals forces between the As-S-As linkages in actual solids.

During illumination, an electron (e^-) will be excited to the conduction band, and, accordingly, a hole (h^+) will be formed in the valence band. In other words, charged (negatively and/or positively) defects will be formed as a result of band-gap illumination. This indicates that at the moment of illumination, weak interlayer interactions or van der Waals forces, which will not be fully taken into account in the present cluster models, will change to a stronger Coulomb interaction. This stronger interaction will be reasonably modeled by the cluster approach because of its localized character as pointed out earlier, and the present cluster calculations are likely to capture some fundamental features of the photostructural changes induced by the photoionization process in the corresponding noncrystalline solids.

When the atoms in model 1 are involved in the process, the photoabsorption event can be written as



where model 2(-) and model 2(+) indicate the photoinduced negatively and positively charged centers, respectively. To investigate the structure of these photoinduced centers, we then obtained the equilibrium geometries of the negatively charged (As₃S₈H₇)⁻ and positively charged (As₃S₈H₇)⁺ clusters at the unrestricted HF (UHF)/6-31G(d) level.

First, we analyze the optimized geometry of model 2(-) [see Fig. 2(a)]. We see from Fig. 2(a) that trapping of an electron induces the breaking of one of the As-S bonds in the cluster, forming a two-coordinated As unit and a nonbridging S atom. Such a bond-breaking mechanism upon illumination has been previously proposed by Elliott [8]. The electron affinity is calculated to be 1.64 eV, which is defined as the total energy difference between model 1 and model 2(-). This positive value of electron affinity indicates that such a moiety as shown in Fig. 1 (model 1) is apt to trap an electron, followed by breaking of one of the As-S bonds. Tachibana *et al.*

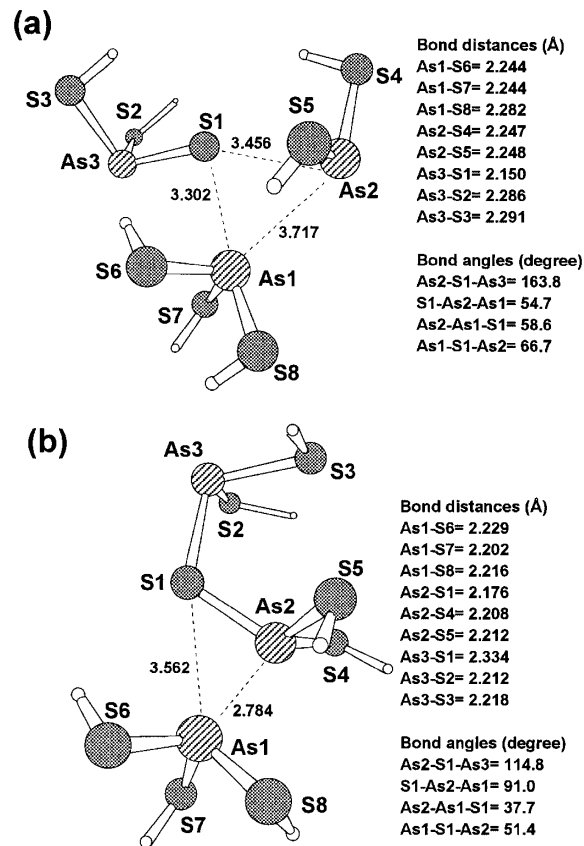


FIG. 2. Optimized geometry of (a) the (As₃S₈H₇)⁻ [model 2(-)] and (b) the (As₃S₈H₇)⁺ [model 2(+)] clusters calculated at the UHF/6-31G(d) level. Principal intramolecular and intermolecular (dashed lines) distances and bond angles are shown. The average intramolecular As-S bond distances of models 2(-) and 2(+) are 2.249 and 2.223 Å, respectively.

[17] previously suggested that the As₄S₆ “casket” will also act as an electron-trapping center in α -As₂S₃; however, breaking of the As-S bond was not predicted by their model. Mulliken total atomic charges q and spin densities ρ calculated for model 2(-) are shown in Table I. It is clear from Table I that the trapped electron is mainly located at the nonbridging S site ($q_{\text{S1}} = -0.621$), leaving an unpaired electron at the two-coordinated As site ($\rho_{\text{As2}} = 1.012$). Table I also shows that the unpaired electron on As2 consists mainly (96%) of p -type wave functions.

We next turn our attention to the positively charged center, model 2(+) [see Fig. 2(b)]. One sees from Fig. 2(b) that in model 2(+), two As atoms (As1 and As2) come together to form a weak As-As bond ($d_{\text{As1-As2}} = 2.784$ Å). In contrast to model 2(-), the spin density of the unpaired electron in model 2(+) is almost equally distributed between the two As atoms (As1 and As2) forming a pair, showing considerable s - p hybridization in the wave function (see Table I). In actual α -As₂S₃, holes are the major mobile carriers, and electrons are quite immobile [18]. Thus, it is most likely that the present positively charged center tends to recombine with an electron, followed by a radiative recombination (photoluminescence) or a

TABLE I. Calculated Mulliken atomic charges q , spin densities ρ , and first singlet-to-singlet ($S_0 \rightarrow S_1$) excitation energies (in eV).

	Model 1	Model 2(-)	Model 2(+)	Model 3
	q	q	ρ	q
As1	0.131	0.167	-0.002	0.039
As2	0.156	0.164	1.012 ^a	0.069
As3	0.139	0.112	0.016	0.209
S1	-0.178	-0.621	-0.011	-0.107
$S_0 \rightarrow S_1$ ^d	3.64	2.56

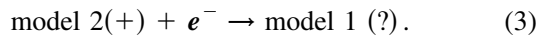
^as-type orbitals 1%, p-type orbitals 96%, and d-type orbitals 3%.

^bs-type orbitals 41%, p-type orbitals 57%, and d-type orbitals 2%.

^cs-type orbitals 28%, p-type orbitals 71%, and d-type orbitals 1%.

^dThe calculations were performed at the TD-DFRT/6-31 + $G(d)$ level using the HF/6-31G(d) geometries.

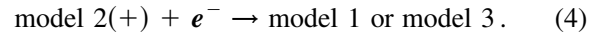
nonradiative process:



To confirm whether the above reaction indeed occurs or not, we reoptimized the geometry of model 2(+) by assuming that the total charge of the cluster is zero. In contrast to the expectation, however, the resultant optimized geometry of the cluster, which is referred to as model 3 (see Fig. 3), is considerably different from that of model 1; the total energy of model 3 is higher than that of model 1 by 1.01 eV. In model 3, one finds two types of coordination defect centers. One is a two-coordinated As unit similar to that shown in model 2(-), and the other is a four-coordinated As unit having a trigonal bipyramidal structure. It should be noted, however, that a substantial As-As bond ($d_{\text{As1-As2}} = 2.463 \text{ \AA}$) is formed between the above two structural units; the bond overlap population for the As1-As2 bond is calculated to be 0.425, which is comparable to that of the usual As-S bond (~ 0.42) in model 1. Thus, a better description for the coordination defects obtained is a fivefold coordinated As unit having four As-S bonds and one As-As bond. To our knowledge, this is the first theoretical calculation showing a possible formation

mechanism of such a fivefold coordinated site in α -As₂S₃ on illumination and the subsequent recombination.

The present calculated results hence demonstrate that during the trapping of an electron, model 2(+) can be transformed into model 3 as well as model 1, depending on the configurational coordinates of the surrounding atoms of the charged center; that is, reaction (3) should be written as



A similar recombination mechanism can also be applied to model 2(-),



although model 2(-) is expected to be more stable against recombination than model 2(+).

We used the time-dependent density-functional response theory (TD-DFRT) [19] to calculate the excitation energies of models 1 and 3. The TD-DFRT excitation energies were calculated for the HF/6-31G(d) geometry at the Becke's hybrid exchange functional with the Lee-Yang-Parr correlation energy functional [20] level with the 6-31G(d) basis set augmented by one set of diffuse functions on As and S atoms [21]. The calculated singlet-to-singlet excitation energies are listed in Table I. We see from Table I that the singlet-to-singlet excitation energy calculated for model 3 (2.56 eV) is appreciably smaller than that for model 1 (3.64 eV). The present calculations strongly suggest that when such a coordination defect as shown in model 3 is formed, an additional absorption band arises at ~ 2.6 eV. Eguchi *et al.* [22] demonstrated that the lower energy shift of the optical band gap of α -As₂S₃ (~ 2.4 eV) by ~ 0.1 eV on illumination results from the appearance of a new absorption band at ~ 3 eV at the expense of a decrease in the absorption above ~ 4 eV. The energy of the photoinduced absorption band (~ 3 eV) is in reasonable agreement with the first excitation energy of model 3 (~ 2.6 eV), suggesting that the formation of the fivefold coordinated As site is responsible for the observed photodarkening.

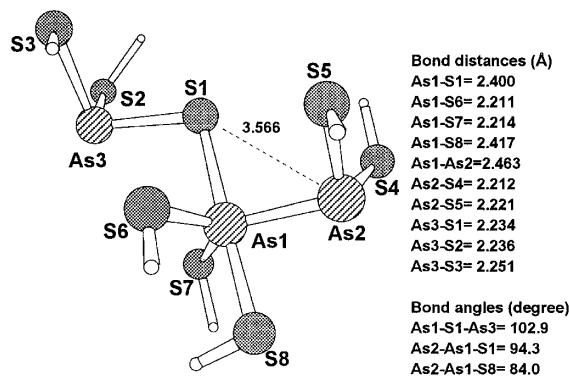


FIG. 3. The higher energy form of the As₃S₈H₇ cluster, model 3, calculated at the HF/6-31G(d) level. Principal intramolecular and intermolecular (dashed lines) distances and bond angle are shown. The average intramolecular As-S bond distance is 2.266 Å.

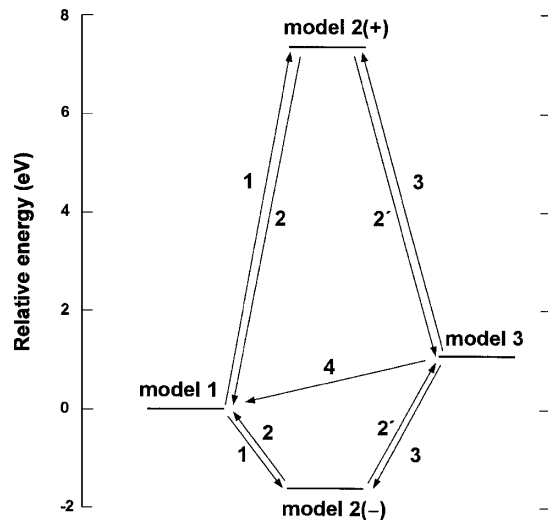


FIG. 4. Energy-level diagram obtained for the neutral and charged model clusters. The energy scale is relative to the total energy of model 1. Transitions 1 and 3 represent photoabsorption steps. Transitions 2 (or 2') and 4 stand for recombination and thermal relaxation steps, respectively.

Finally, we summarize the photostructural change in α -As₂S₃, proposed above, in the energy-level diagram shown in Fig. 4. On band-gap illumination, band-to-band transitions occur (transition 1, Fig. 4), and model 1 is transformed into the positively [model 2(+)] and negatively charged [model 2(-)] centers according to reactions (1) and (2) [23]. These photoinduced charged centers will undergo radiative and/or nonradiative recombinations [24], resulting in the original configuration (transition 2) or a metastable coordination defect (transition 2') according to reaction (4) [or (4')]. Since the singlet-to-singlet excitation energy of model 3 is considerably smaller than that of model 1, photodarkening can possibly occur as a result of the photoabsorption process associated with model 3 (transition 3). The total energy of model 3 is higher than that of model 1 by ~ 1 eV, and the atomic configurations in model 3 will hence be eventually transformed into those in model 1 after annealing near the glass-transition temperature (transition 4). Thus, we conclude that the observed reversible photodarkening behavior during the illumination-annealing cycle may be interpreted in terms of a structural interconversion between models 1 and 3.

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- [23] As shown in Table I, models 2(+) and 2(-) have paramagnetic As centers, which probably correspond to the two types of optically induced electron-spin resonance centers observed for α -As₂S₃ [3,4]. It has been found that the observed As-related paramagnetic centers consist of an electron in a nonbonding *p*-type wave function of a twofold-coordinated As atom (As_{II}) and an electron on an *s-p* hybridized orbital delocalized over more than a single As atom (As_I) [4]. These experimental results are in accordance with the calculated results shown in Table I.
- [24] This implies that, as for radiative recombination of model 2(+), there are two recombination channels, which lead to two different configurations, namely, models 1 and 3. We suggest that these two types of radiative recombination channels are responsible for the observed two photoluminescence bands at ~ 1.1 (PL1) and ~ 0.85 (PL2) eV [1]. The observed fatigue of the PL1 band accompanied by the appearance of the PL2 band [1] may hence be due to a gradual predominance of the photo-induced recombination channel associated with model 3 (rather than model 1) on illumination.

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